

Rolling Process for Producing Biaxially Textured Substrates

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FIELD OF THE INVENTION

The present invention relates to processes of making biaxially textured substrates that include rolling steps, and more particularly to such processes wherein shear force is introduced into the process in order to avoid the need for annealing steps to produce a sharp biaxial texture, and other attributes such as fine grain sizes and elongated grains.

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BACKGROUND OF THE INVENTION

High critical current density conductors fabricated by epitaxial deposition of high temperature superconductors on biaxially textured substrates is considered to be a viable route towards realizing low cost, high performance superconducting wires for a variety of applications. A well-formed cube texture – a biaxially textured face centered cubic (FCC) crystalline structure – is first developed in a metal (pure metal or metal alloy) substrate (template), followed by epitaxial deposition of intermediate oxide buffer layers and superconductors.

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The following U.S. Patents are expressly referenced, and the entire disclosure of each listed patent is expressly incorporated herein by reference:

U.S. Patent No. 6,486,100 issued on November 26, 2002 to Goyal, et al., entitled Method for Preparing Preferentially Oriented, High Temperature Superconductors using Solution Reagents.

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U.S. Patent No. 6,468,591 issued on October 22, 2002 to Goyal, et al., entitled Method For Making MgO Buffer Layers on Rolled Nickel or Copper as Superconductor Substrates.

U.S. Patent No. 6,451,450 issued on September 17, 2002 to Feenstra, et al., entitled
5 Method of Depositing a Protective Layer Over a Biaxially Textured Alloy Substrate and Composition Therefrom.

U.S. Patent No. 6,447,714 issued on September 10, 2002 to Goyal, et al., entitled Method for Forming Biaxially Textured Articles by Powder Metallurgy.

U.S. Patent No. 6,440,211 issued on August 27, 2002 to Beach, et al., entitled Method
10 of Depositing Buffer Layers on Biaxially Textured Metal Substrates.

U.S. Patent No. 6,399,154 issued on June 4, 2002 to Feenstra, et al., entitled Laminate Article.

U.S. Patent No. 6,375,768 issued on April 23, 2002 to Goyal, entitled Method for Making Biaxially Textured Articles by Plastic Deformation.

U.S. Patent No. 6,331,199 issued on December 18, 2001 to Goyal, et al., entitled
15 Biaxially Textured Articles formed by Powder Metallurgy.

U.S. Patent No. 6,270,908 issued on August 7, 2001 to Feenstra, et al., entitled Rare Earth Zirconium Oxide Buffer Layers on Metal Substrates.

U.S. Patent No. 6,261,704 issued on July 17, 2001 to Goyal, et al., entitled MgO
20 Buffer Layers on Rolled Nickel or Copper as Superconductor Substrates.

U.S. Patent No. 6,256,521 issued on July 3, 2001 to Goyal, et al., entitled Preferentially Oriented, High Temperature Superconductors by Seeding and a Method for their Preparation.

U.S. Patent No. 6,235,402 issued on May 22, 2001 to Beach, et al., entitled Buffer
25 Layers on Biaxially Textured Metal Substrates.

U.S. Patent No. 6,180,570 issued on January 30, 2001 to Goyal, entitled Biaxially Textured Articles formed by Plastic Deformation.

U. S. Patent No. 6,159,610 issued on December 12, 2000 to Goyal, et al., entitled Buffer Layers on Metal Surfaces having Biaxial Texture as Superconductor Substrates.

5 U.S. Patent No. 6,156,376 issued on December 5, 2000 to Goyal, et al., entitled Buffer Layers on Metal Surfaces having Biaxial Texture as Superconductor Substrates.

U.S. Patent No. 6,150,034 issued on November 21, 2000 to Goyal, et al., entitled Buffer Layers on Rolled Nickel or Copper as Superconductor Substrates.

10 U.S. Patent No. 6,114,287 issued on September 5, 2000 to Goyal, et al., entitled Method of Deforming a Biaxially Textured Buffer Layer on a Textured Metallic Substrate and Articles Therefrom.

U.S. Patent No. 6,106,615 issued on August 22, 2000 to Goyal, et al., entitled Method of Forming Biaxially Textured Alloy Substrates and Devices Thereon.

15 U.S. Patent No. 6,077,344 issued on June 20, 2000 to Beach, et al., entitled Sol-Gel Deposition of Buffer Layers on Biaxially Textured Metal Substances.

U.S. Patent No. 5,968,877 issued on October 19, 1999 to Budai, et al., entitled High Tc YBCO Superconductor Deposited on Biaxially Textured Ni Substrate.

U.S. Patent No. 5,964,966 issued on October 12, 1999 to Goyal, et al., entitled Method of Forming Biaxially Textured Alloy Substrates and Devices Thereon.

20 U.S. Patent No. 5,958,599 issued on September 28, 1999 to Goyal, et al., entitled Structures Having Enhanced Biaxial Texture.

U.S. Patent No. 5,898,020 issued on April 27, 1999 to Goyal, et al., entitled Structures Having Enhanced Biaxial Texture and Method of Fabricating Same.

25 U.S. Patent No. 5,846,912 issued on December 8, 1998 to Goyal, et al., entitled Method for Preparation of Textured YBa₂Cu₃O_x Superconductor.

U.S. Patent No. 5,741,377 issued on April 21, 1998 to Goyal, et al., entitled Structures Having Enhanced Biaxial Texture and Method of Fabricating Same.

U.S. Patent No. 5,739,086 issued on April 14, 1998 to Goyal, et al., entitled Structures Having Enhanced Biaxial Texture and Method of Fabricating Same.

5 U.S. Patent Application Serial No. 09/406,190 filed on September 27, 1999 by Norton, et al., entitled Buffer Architecture for Biaxially Textured Structures and Method of Fabricating Same.

In the above-taught processes of making biaxially textured substrates, typically a cube
10 texture is formed by rolling and subsequently annealing a metallic preform, usually a metal strip. The as-rolled metal or alloy strip has a rolling texture, which is a complex mixed texture. Annealing of the metal strip is required to form a recrystallization texture, which for FCC metals is the cube texture. High annealing temperatures are generally required in order to form the desired completely cubic texture. Moreover, the resulting
15 grain sizes are also large; the dimensions thereof often approach the thickness of the thin strip. For example, a 50 μm thick substrate, upon complete annealing may often result in a substrate with an average grain size of 50 μm . Furthermore, the grains in a cube-textured strip are generally equiaxed, which is typical of the recrystallization process. A fully annealed, cube textured strip is generally mechanically much softer and weaker compared
20 to the as-rolled strip.

For some applications, it is essential that a fully developed cube texture be formed. For many FCC metals and alloys however, this may require a very high annealing temperature. In some cases upon annealing at high temperatures results in secondary recrystallization of
25 the material and even the previously formed cube texture at lower temperatures is destroyed.

There may be some fundamental limitations towards the fabrication of high- J_c conductors on such templates. One such limitation may be caused by large grain sizes in the substrates with respect to finite width of the substrates, a phenomenon known as
5 percolative pinch-off. The number of grains that exist across the width of a substrate tape is somewhat proportional to the ability of epitaxial superconductors to carry current (J_c), to a point.

Reductions in J_c due to the finite width of the substrate become a less significant negative
10 factor for substrates having a width of at least 100 grains. Hence, for substrates that are at least 0.5 cm (100 grains) wide and have a typical average grain size of no more than 50 μm , the percolative pinch-off of J_c due to a large grain size in the substrate and a finite width of the substrate is less of an issue.

15 However, for many large-scale applications of superconducting materials, substrate widths of 0.4 cm and even less are required. In these cases, the percolative pinch-off of J_c due to a large grain size in the substrate and a finite width of the substrate is a significant issue.

OBJECTS OF THE INVENTION

20 Accordingly, objects of the present invention include the provision of new methods of making biaxially textured substrates wherein post-rolling heating steps can be reduced or eliminated. The invention provides a method of making substrates with fine grain sizes and/or elongated grains. The invention also provides a method of making textured substrates that are harder and/or stronger than annealed substrates. The invention provides a method of

making a biaxially textured substrate with a new kind of biaxial texture. Further and other objects of the present invention will become apparent from the description contained herein.

SUMMARY OF THE INVENTION

5 In accordance with one aspect of the present invention, the foregoing and other objects are achieved by a biaxially textured article that includes a directionally rolled, biaxially textured metallic substrate having an as-rolled, rotated cube texture wherein a (100) cube face thereof is parallel to a surface of said article, and wherein a [100] direction thereof is at an angle of at least 10° relative to a rolling direction thereof, the substrate having
10 thereon at least one epitaxial layer of another material.

In accordance with another aspect of the present invention, a method of preparing a biaxially textured article includes the steps of: rolling a metal preform while applying shear force thereto to form as-rolled biaxially textured substrate having an a rotated cube texture
15 wherein a (100) cube face thereof is parallel to a surface of said substrate, and wherein a [100] direction thereof is at an angle of at least 10° relative to a rolling direction; and depositing onto the surface of the biaxially textured substrate at least one epitaxial layer of another material to form a biaxially textured article.

20 BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic illustration of a high-tension method of applying shear force to produce a biaxially textured article in accordance with the present invention.

Fig. 2 is a schematic illustration of a pulling method of applying shear force to produce a
25 biaxially textured article in accordance with the present invention.

Fig. 3 is a schematic illustration of a method of applying shear force using incongruent rolls to produce a biaxially textured article in accordance with the present invention.

- 5 Fig. 4 is a schematic illustration of a method of applying shear force using offset rolls to produce a biaxially textured article in accordance with the present invention.

Fig. 5a is a log-scale (111) pole figure of as-rolled Cu in accordance with the present invention.

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Fig. 5b is a linear-scale (111) pole figure of as-rolled Cu in accordance with the present invention.

Fig. 6a is a log-scale (200) pole figure of as-rolled Cu in accordance with the present
15 invention.

Fig. 6b is a linear-scale (200) pole figure of as-rolled Cu in accordance with the present invention.

- 20 Fig. 7a is a log-scale (220) pole figure of as-rolled Cu in accordance with the present invention.

Fig. 7b is a linear-scale (220) pole figure of as-rolled Cu in accordance with the present invention.

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Fig. 8 is a (111) phi-scan of as-rolled Cu in accordance with the present invention.

Fig. 9 is a (111) omega-scan of as-rolled Cu in accordance with the present invention.

5 Fig. 10a is a (111) contour pole figure obtained by electron backscatter Kikuchi diffraction of the top surface of as-rolled Cu in accordance with the present invention.

Fig. 10b is a (100) contour pole figure obtained by electron backscatter Kikuchi diffraction of the top surface of as-rolled Cu in accordance with the present invention.

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Fig. 10c is a (110) contour pole figure obtained by electron backscatter Kikuchi diffraction of the top surface of as-rolled Cu in accordance with the present invention.

15 Fig. 11 is an image created by electron backscatter Kikuchi diffraction of the top surface of as-rolled Cu in accordance with the present invention.

For a better understanding of the present invention, together with other and further objects, advantages and capabilities thereof, reference is made to the following disclosure and appended claims in connection with the above-described drawings.

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DETAILED DESCRIPTION OF THE INVENTION

By applying shear force during the rolling process, a biaxially textured substrate can be obtained in an as-rolled state without the need for any annealing. The as-rolled texture has
25 adequate, single orientation, biaxial texture. Shear force can be introduced in one or more of

a variety of ways. The concept of applying shear force to the preform during the rolling process to obtain an as-rolled uniaxial or biaxial texture (with no annealing being necessary) is critical to the invention; the particular method of applying the shear force is not critical to the invention.

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A unique and distinct characteristic of substrates produced in accordance with the present invention is that the textured substrate has a rotated cube texture such that the (100) cube face is parallel to the tape surface and the [100] direction is at an angle of at least 10° relative to the rolling direction. The cube texture is characterized by a $\{100\}\langle 100 \rangle$ orientation which is at an angle of at least 10° relative to an ideal cube texture orientation of $\{100\}\langle 100 \rangle$. The angle is usually about 45°, but can be any angle of 10° or more, for example, 15°, 20°, 25°, 30°, 35°, or 40°. A substrate with an ideal cube texture orientation of $\{100\}\langle 100 \rangle$ is a substrate wherein the (100) planes of all the grains are perfectly parallel to the tape surface and the [100] directions of all the grains are perfectly aligned along the length of a tape. This corresponds to a [100] direction being aligned with the rolling direction.

Biaxially textured substrates made in accordance with the present invention are preferably characterized by an in-plane texture with a x-ray diffraction phi scan peak of no more than 20° full width at half maximum (FWHM) and also by a out-of-plane texture with a omega scan of no more than 20° FWHM (a characteristic of uniaxial texture). FWHM is defined by a Gaussian fit to a line scan such as a phi-scan or a omega scan.

Another unique and distinct characteristic of substrates produced in accordance with the present invention is that the biaxially textured substrate can have an average grain size of

10 μm or less. Preferably, the average grain size thereof is not more than 5 μm , and more preferably not more than 1 μm . The grains preferably have an aspect ratio of at least 10.

The following methods of applying shear force during the rolling process are set forth as
5 examples. These methods and other methods can be used alone or in combination in order to carry out the present invention.

High Tension

As shown in Fig. 1, high tension, or pulling force 14, is applied to a metal strip 10 in front
10 of the rolls 12, 12', resulting in a shear force along the rolling direction, shown by outline arrow. Normal back tension 16 can optionally be applied.

Pulling

As shown in Fig. 2, pulling 24 the metal strip 20 through a set of freely rotating, un-
15 powered rolls 22, 22' results in a shear force along the rolling direction, shown by outline arrow. Normal back tension 26 can optionally be applied.

Reduced Lubrication

Application of a reduced amount of lubricant or no lubricant during rolling results in a
20 shear force along the rolling direction.

Incongruent Rolls

As shown in Fig. 3, using rolls 32, 34 of different diameter so that the circumferential velocities of the work rolls are different results in a shear force applied to the metal strip

30 along the rolling direction, shown by outline arrow. Normal back tension 36 can optionally be applied.

Offset Rolls

- 5 As shown in Fig. 4, the use of offset rolls 42, 44 (in different vertical planes, 46, 48, respectively), results in a shear force applied to the metal strip 40 along the rolling direction, shown by outline arrow. Normal back tension 49 can optionally be applied.

Altered Preform Composition

- 10 Incorporation of rigid particles into a soft ductile metal/alloy matrix results in a composite that undergoes local shear deformation upon rolling. Examples of rigid particles include Al_2O_3 , CeO_2 , YSZ, Y_2O_3 , MgO, and other oxides, nitrides, carbides. Examples of soft ductile metal/alloy matrices include Ni, Cu, Al, Fe, and alloys based thereon.

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EXAMPLE I

A 1" wide, 0.5" thick, 6" long copper bar containing 15 wt% Al_2O_3 in the form of submicron particles was rolled into a biaxially textured tape 50 μm thick and about 1" wide by hand rolling using reduced lubrication and high tension as described above and under the following conditions.

- 20 Rolling temperature: Room temperature

Rolling speed: 15 ft./hr.

Reduction Per Pass: 10%

Rolling direction: Reverse

Applied forward tension: High

- 25 Applied back tension: None

Lubrication: None

Purity of Cu – Oxygen-free

Figs. 5a and 5b show log-scale and linear-scale (111) pole figures of as-rolled Cu
5 fabricated in accordance with Example I. Figs. 6a and 6b show log-scale and linear-scale
is (200) pole figures of the same material, confirming the presence of a strong (200)
texture normal to the surface of the as-rolled tape. Figs. 7a and 7b show log-scale and
linear-scale (220) pole figure of the same material. Fig. 8 is a (111) phi-scan of the tape
showing the in-plane texture and Fig. 9 is an omega-scan showing the out-of-plane texture.
10 These data clearly show the presence of a biaxially textured, 45°-rotated cube texture in
the material.

Figs. 10a, 10b, and 10c are, respectively, (111), (100), and (110) electron backscatter
Kickuchi diffraction pole figures of the top surface of the tape. Clearly a clean, 45°-
15 rotated cube texture in the material is seen at the top surface. The additional peaks in the
pole figures are attributable to the material in the interior of the tape.

Fig. 11 shows the microstructure of the same region from which the data for Figs. 10a,
10b, and 10c were taken. Different shades of gray represent single grains. A grain is
20 defined as a percolatively connected region within 3 degrees. Fig. 11 shows that the
grains at the surface of the tape are elongated and form a “brick-floor” microstructure
which is advantageous for supporting high-quality electromagnetic and electro-optical
devices, especially high-temperature superconductors.

A “brick-floor” microstructure is defined as follows: The surface of the tape has aspected (elongated) grains having an aspect ratios of at least 10 in the plane of the substrate and having at least one crystallographic direction in the grains aligned. The aspect ratio is defined as the ratio of the length of the grain divided by the width of the grain in the plane of the substrate. With respect to texture, in cases where only one crystallographic axis is preferentially aligned (uniaxial texture), then the aligned axis is the crystallographic normal or perpendicular to the plane of the tape. In cases where two axes are aligned (biaxial texture), both the axis perpendicular to the tape and an axis in the plane are aligned. In the present invention, a unique and distinct brick floor microstructure with a rotated uniaxial and/or biaxial texture is attainable.

While there has been shown and described what are at present considered the preferred embodiments of the invention, it will be obvious to those skilled in the art that various changes and modifications can be prepared therein without departing from the scope of the inventions defined by the appended claims.